

The Adsorption of Lead from Aqueous Solutions Using Coal Fly Ash : Effect of Crystallinity

Widi Astuti, Agus Prasetya, Endang Tri Wahyuni, I Made Bendiyasa

Abstract—Coal fly ash (CFA) generated by coal-based thermal power plants is mainly composed of some oxides having high crystallinity, like quartz and mullite. In this study, the effect of CFA crystallinity toward lead adsorption capacity was investigated. To get solid with various crystallinity, the solution of sodium hydroxide (NaOH) of 1-7 M was used to treat CFA at various temperature and reflux time. Furthermore, to evaluate the effect of NaOH-treated CFA with respect to adsorption capacity, the treated CFA were examine as adsorbent for removing lead in the solution. The result shows that using NaOH to treat CFA causes crystallinity of quartz and mullite decrease. At higher NaOH concentration (>3M), in addition the damage of quartz and mullite crystallinity is followed by crystal formation called hydroxysodalite. The lower crystallinity, the higher adsorption capacity.

Keywords—Coal fly ash, crystallinity, lead, adsorption capacity

I. INTRODUCTION

LARGE quantities of fly ash are produced during the combustion of coal in the production of electricity. In Indonesia, more than 1 million tons of fly ash is being generated annually [9]. Most of this ash is used in low level applications such as landfill. Two approaches have been made for proper utilization of CFA, either to reduce the cost of disposal or to minimize the environmental impact. One application of CFA is used as adsorbent [7].

CFA is mainly composed of some oxides such as Al_2O_3 , SiO_2 and unburned carbon [4] that make it as an adsorbent. High coal combustion temperature often produces Al_2O_3 and SiO_2 having high crystallinity like quartz and mullite. It reduces the adsorption capacity of the CFA. In this study, crystallinity of quartz and mullite will be reduced by reaction with NaOH to form amorphous CFA having high adsorption capacity.

In the environment, Lead (Pb) is one of the major pollutants is mainly discharged from exhaust gases of

automobile to environment. In addition, lead can enter to the water and environment through effluents from lead smelters, battery manufactures, painting, paper and ammunition industries [3]. The concentration of lead ions in the industrial waste waters is in the range of 200-500 $mg.dm^{-3}$ where is very high level concentration to the standard and should be reduced to a range of 0.1-0.05 $mg.dm^{-3}$ before discharge to the environment [3].

Several methods have evolved over the years on the removal of this metal ion present in industrial waste water such as chemical precipitations, coagulation, reverse osmosis, ion exchange and adsorption. Among of these methods, adsorption appears to be the most widely used for the removal of heavy metals [1]. Many adsorbents have been tested to remove it from aqueous solutions including bentonite [3], peat [11] and zeolite [2]. However, to improve the efficiency of adsorption process, it is necessary to develop an adsorbent that is cheaper but has high adsorption capacity such as CFA.

II. MATERIALS AND METHODS

A. Sample Preparation and Characterization

Lead nitrat, $PbNO_3$, used in adsorption experiments is in extra pure grade and was purchased through Merck. pH adjustments were carried out by 0.1M hydrochloric acid (HCl) and 0.1M sodium hydroxide (NaOH).

CFA was obtained from Tanjungjati power plant, Jepara, Indonesia. Before any treatment, it was washed with deionized water, dried and sieved through a BSS Tyler Sieve of 100-mesh size. Then, CFA was reacted with various NaOH concentrations (1 to 7M), various temperatures (40 to 90°C) for one to six hours to reduce quartz and mullite crystallinity in a batch reactor. The ratio of CFA weight to NaOH was 1 gram of CFA to 6 mL of NaOH. NaOH-treated CFA was filtered and washed several times with deionized water until pH of the filtrate was around 7, dried, characterized and used as an adsorbent in the sorption experiments. The chemical compositions of original CFA were analyzed using x-ray fluorescence (XRF). X-ray diffraction (XRD) patterns for original and treated CFA were obtained by powder method using Cu $K\alpha$ radiation (Schimadzu XRD-6000). Scanning Electrone Microscopy (SEM) micrographs for original and treated CFA were obtained from SEM (JEOL, Japan). Specific surface area for both original and treated CFA were

W. Astuti is with the Chemical Engineering Department, Semarang State University, Semarang, Indonesia and Ph.D student at the the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: wiewied.unnes@gmail.com).

A. Prasetya is with the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia.

E.T. Wahyuni is with the Chemistry Department, Gadjah Mada University, Yogyakarta, Indonesia.

I M. Bendiyasa is with the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia.

measured by N₂ physisorption at 77 K using a NOVA 1200 microanalyzer (QUANTACHROME).

B. Batch Adsorption Experiment

Original or treated CFA (dose varied from 0.1-2.0 g) was put into an erlenmeyer filled 50 mL of lead solution (Lead solution concentrations were varied from 5 to 50 mg.dm⁻³). The adsorption was carried out at pH of 5. The erlenmeyer contained the mixture was placed in a waterbath at 26°C and shaken mechanically for 5 to 180 minutes. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine lead concentration using atomic absorption spectrophotometer (Perkin Elmer).

To investigate the effect of pH on adsorption, 1 g of original or treated CFA was added to an erlenmeyer filled 50 mL of 10 ppm lead solution. The pH was adjusted with base/acid to an appropriate pH (pH range of 3 to 9). The erlenmeyer filled the mixture was placed in a waterbath at 26°C and shaken mechanically for 180 minutes. The ash was separated from the solution and the filtrate was analyzed to determine lead concentration using atomic absorption spectrophotometer (Perkin Elmer).

III. RESULTS AND DISCUSSION

A. Chemical composition

The chemical compositions obtained from x-ray fluorescence (XRF) analysis is presented in Table 1. It shows that the major component of CFA are silica (SiO₂), alumina (Al₂O₃) and carbon. To confirm the existence of silica and alumina, CFA is analyzed using x-ray diffraction (XRD). The XRD pattern of CFA can be seen from Figure 1. It shows that CFA contains crystalline phases including quartz (SiO₂), mullite (3 Al₂O₃ · 2 SiO₂) and amorphous components. Thus, there is suitability between the result of XRF analysis and XRD pattern.

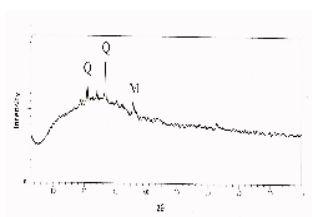


Fig. 1 XRD patterns of tanjungjati fly ash
 Symbols : Q-quartz, M-mullite

B. NaOH treatment

To decrease crystallinity of quartz and mullite, CFA was treated with various NaOH concentration at various temperature and time. The XRD pattern of treated CFA can be seen in Figure 2 and 3. Figure 2 demonstrates that NaOH treatment causes the decrease of quartz and mullite crystallinity, on the other word, the amorphous of quartz and mullite increase. The decrease of quartz and mullite

crystallinity are described by decreasing intensity of peaks at $2\theta = 20.9$; $2\theta = 26.7$ for quartz and $2\theta = 25.9$; $2\theta = 35.2$ for mullite. However, at higher sodium hydroxide concentration, the decreasing of quartz and mullite intensity are followed by formation of hydroxysodalite (1.08 Na₂O · Al₂O₃ · 1.68 SiO₂ · 18 H₂O) indicated by new peaks at $2\theta = 13.9$; $2\theta = 24.2$ and $2\theta = 42.7$. At the same concentration, the higher temperature, the higher hydroxysodalite peaks intensity.

TABLE I
 CHEMICAL COMPOSITION OF TANJUNGGATI FLY ASH

Component	Content (mass %)
SiO ₂	36.47
Al ₂ O ₃	19.27
CaO	6.56
MgO	2.94
Fe ₂ O ₃	10.74
MnO	0.07
Na ₂ O	1.76
K ₂ O	1.77
CuO	0.01
As ₂ O ₃	0.01
P ₂ O ₅	0.25
SO ₃	1.04
Carbon	19.11

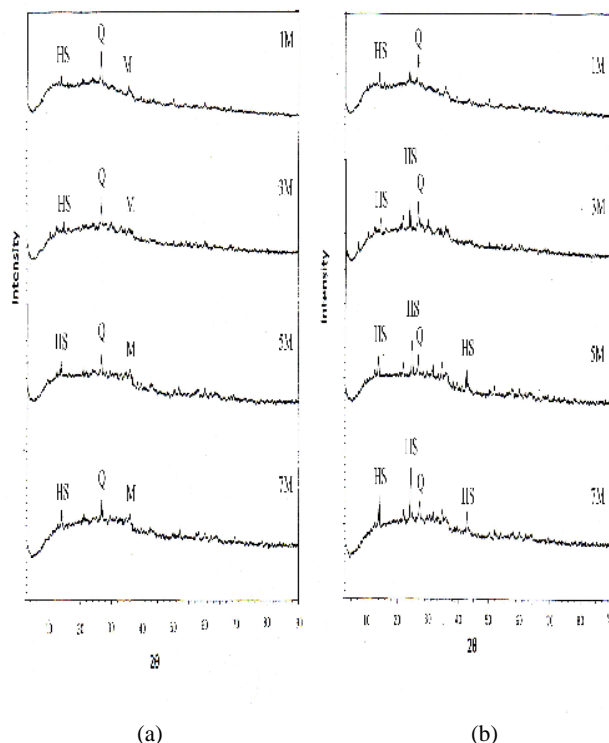


Fig. 2 XRD patterns of NaOH-treated CFA at various NaOH concentration (1-7 M). Reaction time 6 hours : (a) temperature of 60°C, (b) temperature of 90°C. Symbols : Q-quartz, M-mullite, HS-hydroxysodalite

Decreasing quartz and mullite crystallinity without hydroxysodalite formation can be seen in Figure 3. At the range studied, the longer reaction time, the lower quartz and mullite crystallinity and the higher CFA amorphous.

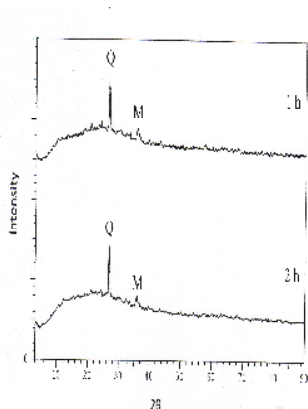
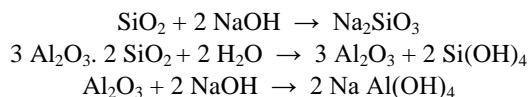


Fig. 3 XRD patterns of NaOH-treated CFA at various reaction time (1 and 2 hours). NaOH concentration of 3M, temperature of 60°C
 Symbols : Q-quartz, M-mullite

Quantitatively, crystallinity of quartz is calculated using comparison between intensity of two peaks of quartz in treated CFA with quartz standard. Crystallinity of mullite and hydroxysodalite are calculated using comparison between intensity of three peaks of them in treated CFA with mullite and hydroxysodalite standard, which can be written [10] :

$$\text{crystallinity} = \frac{I_A}{I_c} \times 100 \quad (1)$$

where I_A is intensity of quartz, mullite or hydroxysodalite in treated CFA and I_c is intensity of standard quartz, mullite or hydroxysodalite. Figure 4 shows the effect of NaOH concentration toward the crystallinity. The higher NaOH concentration, the lower crystallinity of quartz and mullite. NaOH damages quartz and mullite then compose sodium silicate and sodium aluminat, which can be written [5] :



Thus, the higher NaOH concentration, the more quartz and mullite damaged, on the other word, the crystallinity decrease. Nevertheless, the decrease quartz and mullite can be followed by hydroxysodalite formation. At low temperature, it is not significant, but at higher temperature (90°C), the increasing hydroxysodalite crystallinity is very high. The crystallinity of hydroxysodalite increase with increasing NaOH concentration whereas quartz and mullite crystallinity decrease. The hydroxide acts as a strong mineralizing agent which forces the reactants into solution. The greater OH⁻ concentration, the

greater concentration of reactants in solution and thus the greater rate of crystal growth [10].

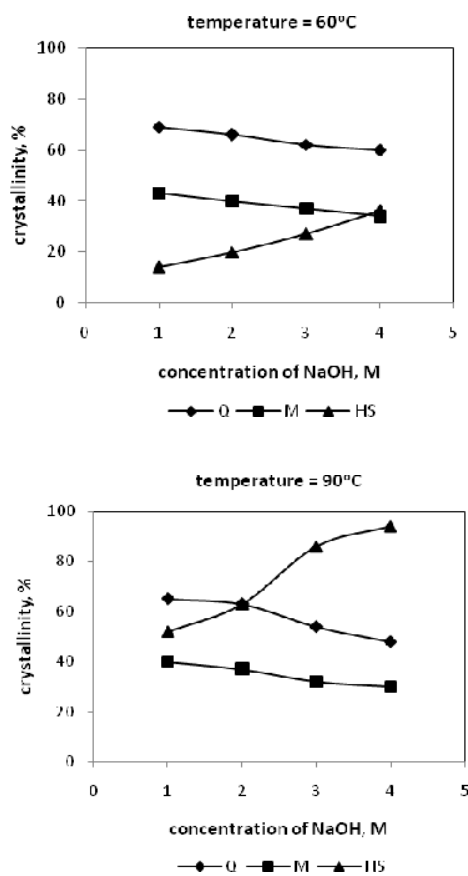


Fig. 4 The effect of NaOH concentration toward CFA crystallinity
 Reaction time : 6 hours.
 Symbols : Q-quartz, M-mullite, HS-hydroxysodalite.
 Crystallinity of original CFA : Q = 88% , M = 71% , HS = 0%

Figure 5 described the effect of reaction time toward the crystallinity. The longer reaction time, the lower quartz and mullite crystallinity. It is because the longer time of quartz and mullite reacted with NaOH, the more quartz and mullite damaged.

Specific surface area of original and treated CFA is described by Figure 6. It shows that original CFA has the lowest surface area. Treatment using NaOH at low concentration and low temperature increase specific surface area, but at higher NaOH concentration and higher temperature, specific surface area decrease because a lot of hydroxysodalite formed. CFA which has highest surface area is produced by treatment using NaOH concentration of 3 M at temperature of 60°C for 2 hours. In this condition, quartz and mullite crystallinity decrease but hydroxysodalite is not formed. There is suitability with XRD pattern.

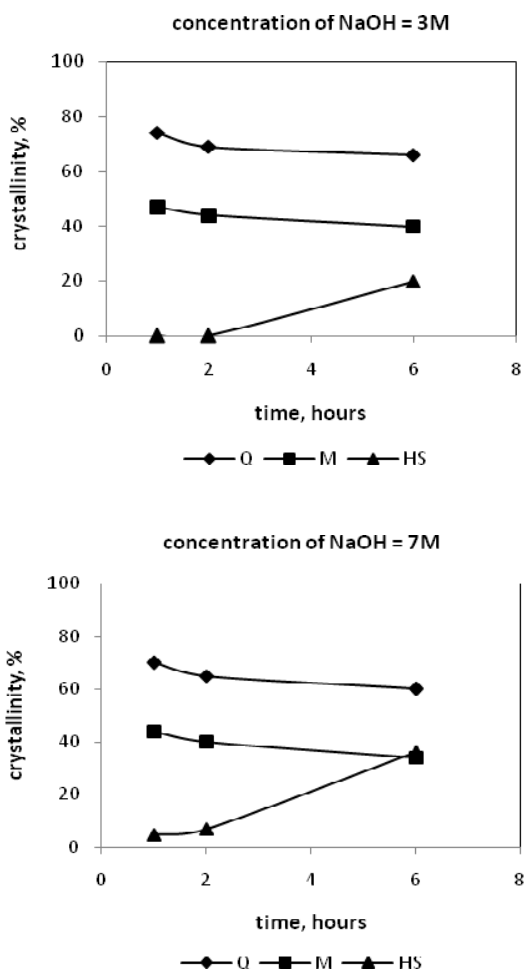


Fig. 5 The effect of reaction time toward CFA crystallinity
 Temperature : 60°C
 Symbols : Q-quartz, M-mullite, HS-hydroxysodalite.
 Crystallinity of original CFA : Q = 88% , M = 71% , HS = 0%

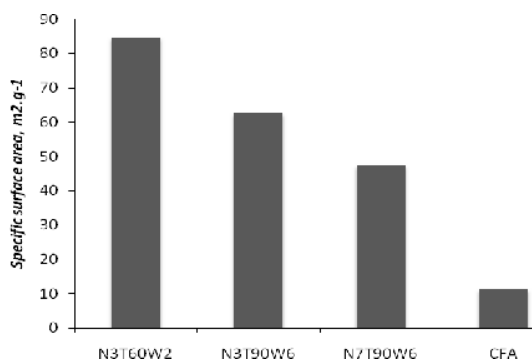


Fig. 6 Specific surface area original and treated CFA
 N3T60W2 means NaOH concentration of 3M, Temperature of 60°C, reaction time of 2 hours

The formation of hydroxysodalite also causes decreasing pore size, as can be seen in Figure 7. At NaOH concentration of 7 M, temperature of 90°C and reaction time of 6 hours, pore diameter is 1.35 nm. It is smaller than original CFA (1.52 nm). Nevertheless, the largest pore diameter is produced by treatment using NaOH concentration of 3 M, temperature of 60°C for 2 hours. It is because increasing amorphous of CFA. The pore size distribution of treated CFA (N3T60W2) can be seen in Figure 8. It shows that most of pore diameter is 14 nm.

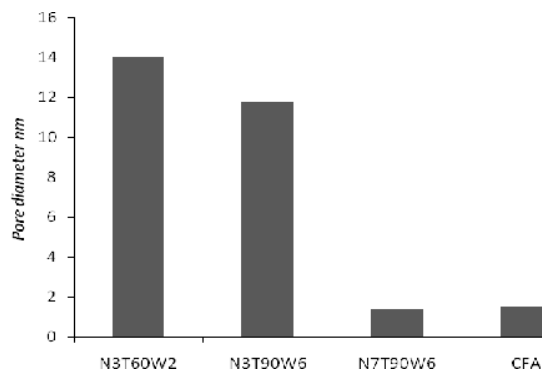


Fig. 7 Pore diameter original and treated CFA
 N3T60W2 means NaOH concentration of 3M, Temperature of 60°C, reaction time of 2 hours

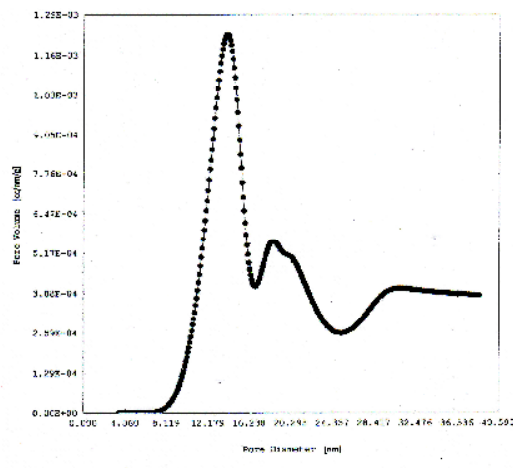


Fig. 8 Pore size distribution of NaOH-treated CFA (concentration of NaOH, reaction time and temperature are 3M, 60°C and 2 hours, respectively)

Figure 9 describes SEM micrograph of original and NaOH treated CFA. Original CFA comprises smooth spherical particles (Figure 9a), while amorphous CFA is indicated by rougher surface and full of holes (Figure 9b). Hydroxysodalite formation decrease the holes and seen a lot of crystal on the surface (Figure 9d). It causes decrease specific surface area and pore size.

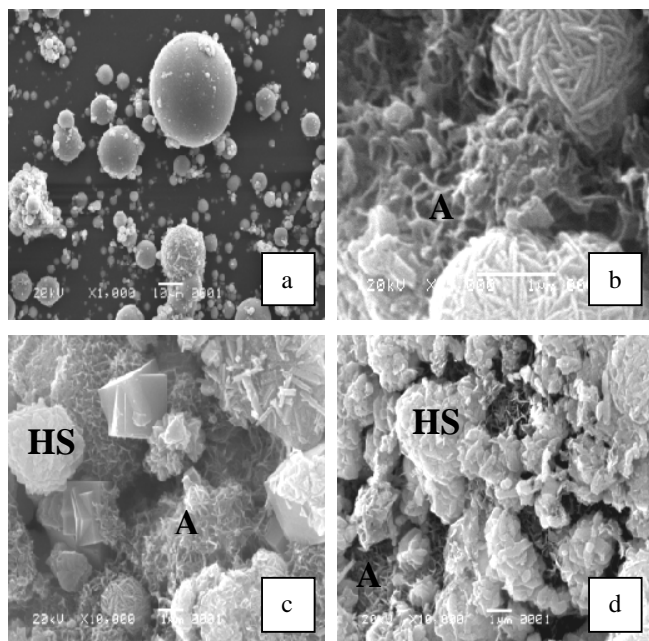


Fig. 9 SEM micrograph of (a) original CFA, (b) treated CFA with reflux by 3M NaOH, 60°C, 2 hours, (c) treated CFA with reflux by 3M NaOH, 90°C, 6 hours, (d) treated CFA with reflux by 7 M NaOH, 90°C, 6 hours. Symbols : HS-hydroxysodalite, A-amorphous

C. Lead Adsorption

1. Effect of Crystallinity

Figure 10 shows that lead adsorbed by original CFA is lower than that of NaOH-treated CFA. It is because NaOH treatment can decrease crystallinity of quartz and mullite or in other words, the amorphous increase. This means, the active sites on metal oxide becomes open, and chemisorption between lead ions and the active site occur easily. CFA contains 69% quartz, 44 % mullite and 0% hydroxysodalite (Q69M44H0) has the highest amorphous. The higher amorphous, the higher lead adsorbed. CFA contains 48% quartz, 30% mullite and 94% hydroxysodalite (Q48M30H94) has lower adsorption capacity because a lot of hydroxysodalite was formed. Hydroxysodalite is a crystal having low specific surface area. As a result, the lead adsorbed decrease. Pb adsorbed decreases with the increasing initial lead concentration and then constant. This is because of equilibrium has been attained.

2. Effect of pH

pH of solution affect surface charge of the adsorbent as well as the degree of ionization of different pollutants. Figure 11 shows the effect of pH on the adsorption of lead ions onto CFA from aqueous solutions. Removal of the lead ions increase until pH 5, and then decreases with the increase of pH. This means, at lower H⁺ concentrations, the CFA surface becomes more negatively charged, so the strongest electrostatic force occurred between fly ash and lead ion at pH 5. At higher H⁺ concentration, competition between H⁺ ion

and lead ion occur, and at pH values higher than 6, metal precipitation occurs, so adsorption lead decreases. As a consequence, the pH chosen for adsorption is 5.

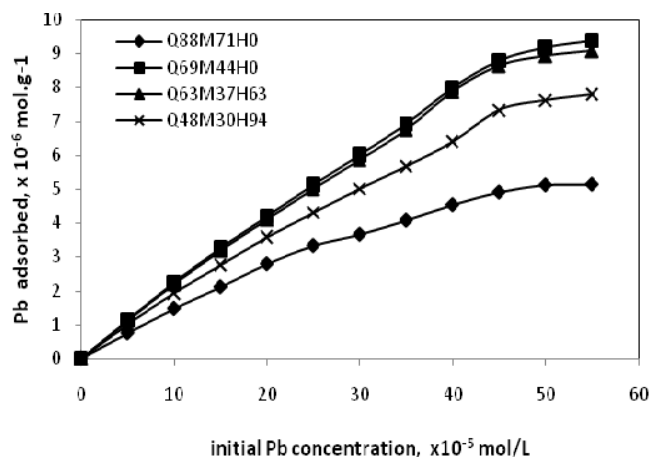


Figure 10 Effect of initial concentration on removal of Pb by original and NaOH-treated CFA (CFA dose = 1g/50 mL solution, reaction time = 180 minutes, pH = 5) symbols are : Q88M71H0 = crystallinity of quartz 88%, mullite 71%, hydroxysodalite 0%

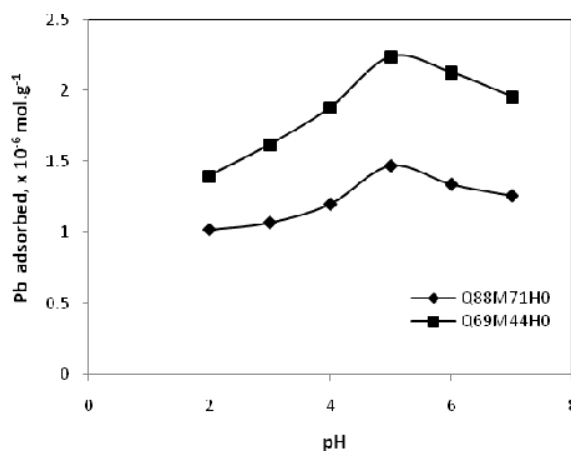


Fig. 11 Effect of pH on Pb adsorption by original and NaOH-treated CFA (CFA dose = 1g/50 mL solution, initial concentration = 10 ppm, reaction time = 180 minutes)

3. Effect of reaction time

In the first few minutes, the adsorbate uptake is very fast and then it becomes slow and finally level off as can be see Figure 12. In the initial stage of adsorption, a large number of vacant surface sites are available for adsorption and after some active sites are occupied by adsorbate, the adsorption process becomes difficult due to repulsive forces between the solute molecules on solid and bulk phases [6].

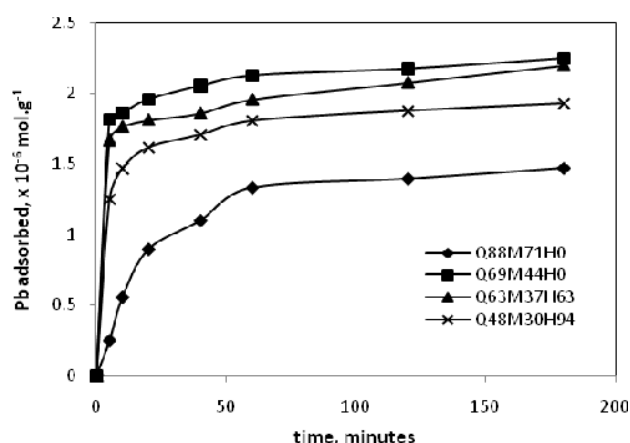


Fig. 12 Effect of reaction time on Pb removal (CFA dose = 1g/50 mL solution, initial concentration = 10 ppm, pH = 5)

D. Adsorption Kinetics

In order to clarify the adsorption kinetics of lead onto CFA, pseudo-first and second order kinetic models were applied to the experimental data. The linearized form of the pseudo first order rate equation by Lagergren is given as [3] :

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are amounts of the lead adsorbed at equilibrium (mol g^{-1}) and at time t (mol g^{-1}), respectively, k_1 is the rate constant (min^{-1}), t is time (min). The adsorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t . Experimental data were also fitted for the pseudo second order [11] :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 ($\text{g} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$) is the rate constant. Equation (3) is solved graphically by plotting t/q_t versus t . The value of q_e can be calculated from the slope of the straight line and k_2 from its intercept. Table 2 illustrates the k_1 and k_2 for pseudo first and second order rate constants as well as q_e for both of them. It indicated that the experimental data fit with the pseudo second order model. It is because chemisorptions occurs involving ionic forces between active site of metal oxide on CFA and lead ions [12].

IV. CONCLUSION

It is concluded that NaOH treatment decrease crystallinity of quartz and mullite, while at higher NaOH concentration, the decreasing of quartz and mullite are followed by formation of hydroxysodalite. The lower quartz and mullite crystallinity, the higher amorphous of CFA and the higher lead adsorbed. It is

because specific surface area increase. The amount of lead adsorbed depends on the initial concentration of lead, pH of solution and contact time. Adsorption kinetics of lead onto CFA could be approximated with pseudo second order kinetic model which the rate constant is $1.97 \times 10^3 \text{ g mol}^{-1} \text{ min}^{-1}$.

TABLE II
PARAMETERS FOR ADSORPTION KINETICS OF LEAD

Pseudo first order		R^2	Pseudo second order		R^2
q_e (mol g^{-1})	k_1 (min^{-1})		q_e (mol g^{-1})	k_2 ($\text{g mol}^{-1} \text{ min}^{-1}$)	
6.3×10^{-7}	0.02	0.652	2.25×10^{-5}	1.97×10^3	0.999

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REFERENCES

- [1] C.D. Woolard, K. Petrus, M.V.D. Horst, "The use of a modified fly ash as an adsorbent for lead", *Water SA*, vol. 26, no. 4, pp.531 – 536, 2000.
- [2] D. Wen, Y.S. Ho, X.Tang, "Comparative sorption kinetics studies of ammonium onto zeolite", *J.Hazard. Mater*, vol. B 113, pp. 252-256, 2006.
- [3] J.A. Hefne, W.K. Mekhemer, N.M. Alandis, O.A. Aldayel, T. Alajyan, "Kinetic and Thermodynamic study of the Adsorption of Pb(II) from Aqueous solution to The Natural and Treated Bentonite", *International Journal of Physical Sciences*, vol. 3, pp. 281-288, 2008.
- [4] J.Y. Hwang, X. Sun, Z. Li, "Unburned Carbon from Fly Ash for Mercury Adsorption : I. Separation and Characterization of Unburned Carbon", *Journal of Minerals and Materials Characterization & Engineering*, vol 1, no. 1, pp. 39-60, 2002.
- [5] K.H. Sugiyarto, *Kimia Anorganik I* (Unpublished Book style). Yogyakarta : Jurusan Pendidikan Kimia Universitas Negeri Yogyakarta , 2000.
- [6] M. Dogan, Y. Ozdemir, M. Alkan, "Adsorption Kinetics and Mechanism of Cationic Methyl Violet and Methylene Blue Dyes onto Sepiolite", *Dyes and Pigments*, vol.75, pp. 701-713, 2007.
- [7] P. Ricou, V. Hequet, I. Lecuyer, P. Le Cloirec, "Removal of Cu^{2+} and Zn^{2+} in Aqueous Solutions by Sorption onto Fly Ash and Fly Ash Mixtures (Published Conference Proceedings style)," in *Proc. International Ash Utilization Symposium*, University of Kentucky, 1999.
- [8] Schneider and Komarneni, *Mullit* (Book style). Wiley-VCH, 2005.
- [9] Sukandarrumidi, *Batubara dan Pemanfaatannya* (Book style). Yogyakarta : Gadjah Mada University Press, 2006.
- [10] Sutarno, "Sintesis Faujasite dari Abu Layang Batubara : Pengaruh Refluks dan penggerusan Abu Layang Batubara terhadap Kristalinitas Faujasite," *Jurnal Matematika dan Sains*, vol.9 no.3, pp.285-290, 2004.
- [11] Y.S. Ho, G. McKay, "Batch Lead (II) Removal from Aqueous Solution by Peat : Equilibrium and Kinetics", *Trans IChemE*, vol. 77 part B, pp. 165-173, 1999.
- [12] Y.S. Ho, "Review of Second-Order Models for Adsorption Systems," *Journal of Hazardous Materials*, B136, pp. 681-689, 2006.

Widi Astuti is Ph.D student at the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia. She also serve as a faculty member at the Chemical Engineering Department, Semarang State University, Semarang, Indonesia. In recent years, she focuses on the application of coal fly ash for adsorbant.